



US009079817B2

(12) **United States Patent**  
**Moser et al.**

(10) **Patent No.:** **US 9,079,817 B2**  
(45) **Date of Patent:** **\*Jul. 14, 2015**

(54) **INITIAL HYDROTREATING OF  
NAPHTHENES WITH SUBSEQUENT HIGH  
TEMPERATURE REFORMING**

USPC ..... 585/300–304, 312, 315, 319, 322, 407,  
585/430, 800, 804, 805  
See application file for complete search history.

(75) Inventors: **Mark D. Moser**, Elk Grove Village, IL  
(US); **David A. Wegerer**, Lisle, IL (US);  
**Manuela Serban**, Glenview, IL (US);  
**Kurt M. VandenBussche**, Lake in the  
Hills, IL (US)

(73) Assignee: **UOP LLC**, Des Plaines, IL (US)

(\*) Notice: Subject to any disclaimer, the term of this  
patent is extended or adjusted under 35  
U.S.C. 154(b) by 264 days.

This patent is subject to a terminal dis-  
claimer.

(21) Appl. No.: **13/327,220**

(22) Filed: **Dec. 15, 2011**

(65) **Prior Publication Data**

US 2013/0158317 A1 Jun. 20, 2013

(51) **Int. Cl.**

**C10G 35/04** (2006.01)  
**C07C 5/02** (2006.01)  
**C07C 15/00** (2006.01)  
**C10G 35/00** (2006.01)  
**C10G 59/00** (2006.01)

(52) **U.S. Cl.**

CPC ..... **C07C 15/00** (2013.01); **C10G 35/00**  
(2013.01); **C10G 59/00** (2013.01); **C10G**  
**2400/30** (2013.01)

(58) **Field of Classification Search**

CPC ..... C07C 5/00; C07C 5/02; C07C 5/03;  
C07C 5/32; C07C 5/321; C07C 5/324; C07C  
5/325; C07C 4/00; C07C 4/02; C07C 4/04;  
C07C 4/06; C10G 35/00; C10G 35/02;  
C10G 35/04; C10G 35/06; C10G 35/085;  
C10G 35/09

(56) **References Cited**

#### U.S. PATENT DOCUMENTS

4,401,554 A \* 8/1983 Choi et al. .... 208/64  
4,508,617 A 4/1985 Montgomery  
5,935,415 A \* 8/1999 Haizmann et al. .... 208/64  
6,004,452 A \* 12/1999 Ash et al. .... 208/80  
6,740,228 B1 \* 5/2004 Verduijn et al. .... 208/138  
2007/0299289 A1 \* 12/2007 Bresler et al. .... 585/323

#### FOREIGN PATENT DOCUMENTS

RU 2417249 C1 4/2011  
WO 1991006616 A2 5/1991

#### OTHER PUBLICATIONS

Sinnott, R.K., Coulson & Richardson's Chemical Engineering,  
Chemical Engineering Design, vol. 6, Fourth Edition, Elsevier, p.  
50.\*

U.S. Appl. No. 13/327,164, filed Dec. 15, 2011, Moser et al.

U.S. Appl. No. 13/327,200, filed Dec. 15, 2011, Moser et al.

(Continued)

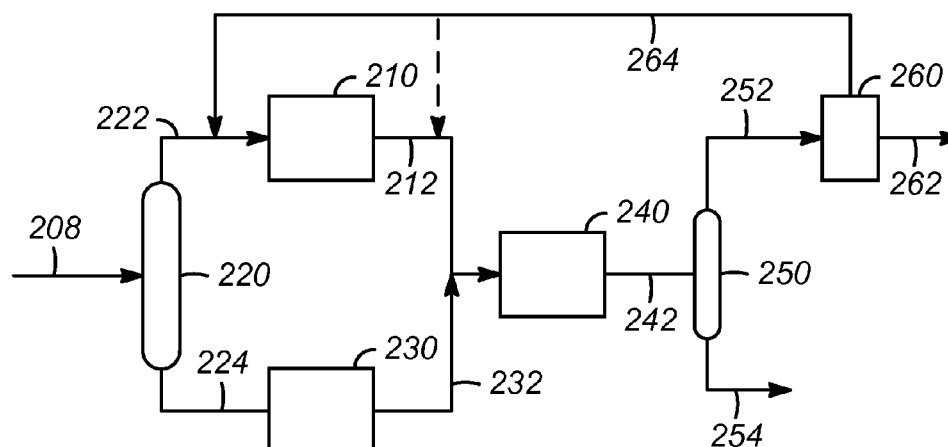
*Primary Examiner* — In Suk Bullock

*Assistant Examiner* — Philip Louie

(57) **ABSTRACT**

A process for the production of aromatics through the reform-  
ing of a hydrocarbon stream is presented. The process utilizes  
the differences in properties of components within the hydro-  
carbon stream to increase the energy efficiency. The differ-  
ences in the reactions of different hydrocarbon components in  
the conversion to aromatics allows for different treatments of  
the different components to reduce the energy used in reform-  
ing process.

**16 Claims, 2 Drawing Sheets**



(56)

**References Cited**

OTHER PUBLICATIONS

U.S. Appl. No. 13/327,143, filed Dec. 15, 2011, Moser et al.  
U.S. Appl. No. 13/327,212, filed Dec. 15, 2011, Moser et al.  
U.S. Appl. No. 13/327,185, filed Dec. 15, 2011, Serban et al.  
U.S. Appl. No. 13/327,178, filed Dec. 15, 2011, Serban et al.  
U.S. Appl. No. 13/327,170, filed Dec. 15, 2011, Serban et al.  
U.S. Appl. No. 13/327,192, filed Dec. 15, 2011, Serban et al.  
U.S. Appl. No. 13/416,513 filed Mar. 9, 2012, Serban.  
U.S. Appl. No. 13/416,702 filed Mar. 9, 2012, Gajda.  
U.S. Appl. No. 13/417,181 filed Mar. 9, 2012, Gajda.  
U.S. Appl. No. 13/417,200 filed Mar. 9, 2012, Wegerer.

U.S. Appl. No. 13/417,202 filed Mar. 9, 2012, Gajda.  
U.S. Appl. No. 13/417,203 filed Mar. 10, 2012, Gajda.  
U.S. Appl. No. 13/440,487 filed Apr. 5, 2012, Moser.  
U.S. Appl. No. 13/440,527 filed Apr. 5, 2012, Moser.  
U.S. Appl. No. 13/440,381 filed Apr. 5, 2012, Moser.  
U.S. Appl. No. 13/428,005 filed Mar. 23, 2012, Serban.  
U.S. Appl. No. 13/416,604 filed Mar. 9, 2012, Serben.  
U.S. Appl. No. 13/416,577 filed Mar. 9, 2012, Negiz.  
PCT International Preliminary Report on Patentability for  
PCTUS2012/055014, mailing date 26 Jun. 2014, Applicant refer-  
ence.

\* cited by examiner

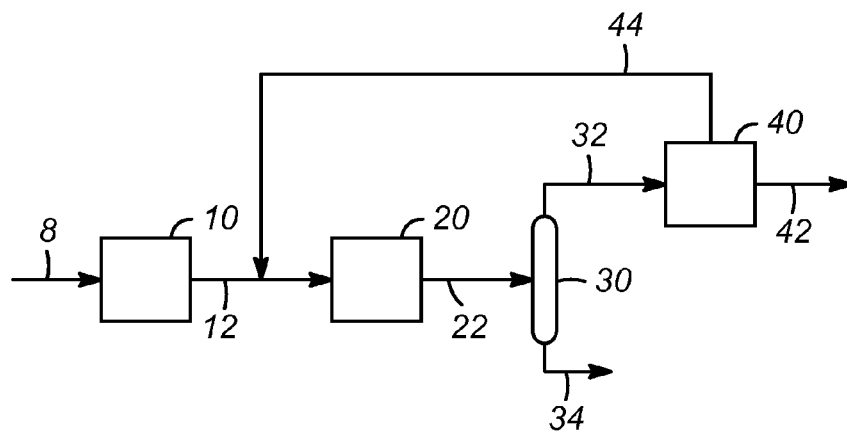


FIG. 1

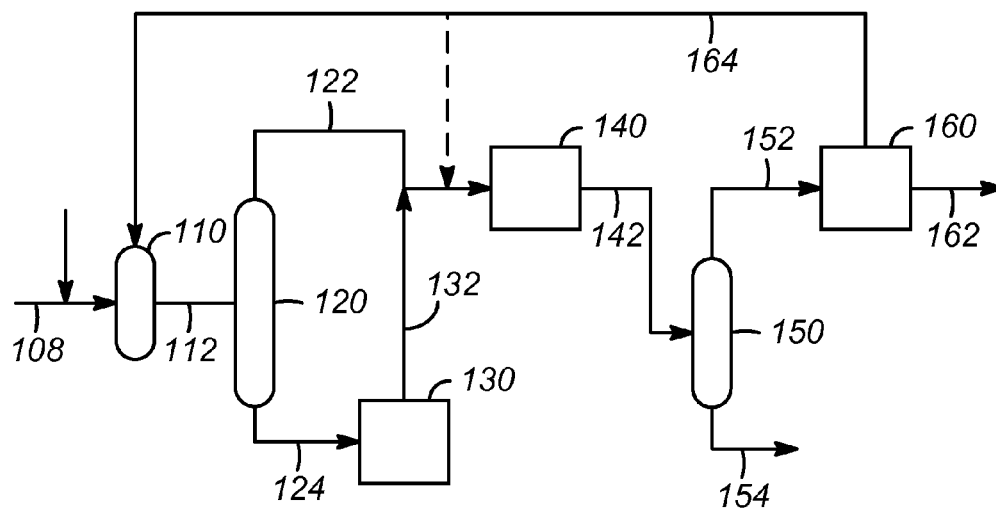


FIG. 2

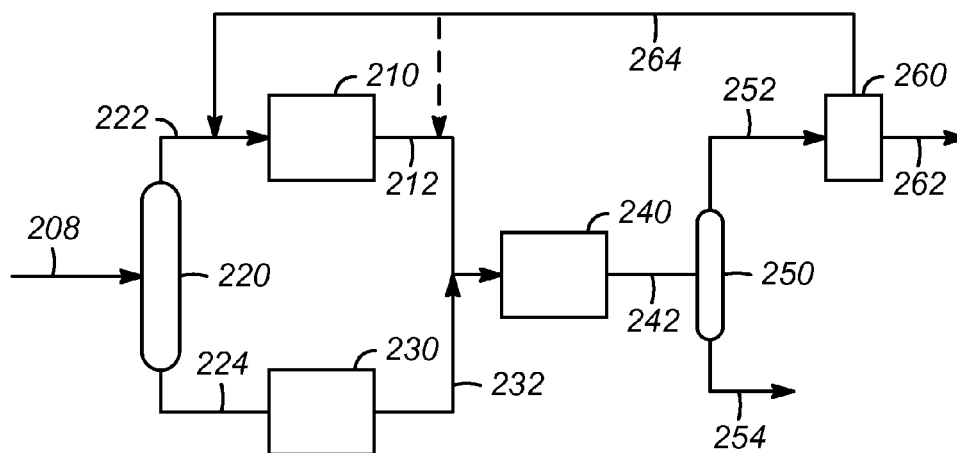


FIG. 3

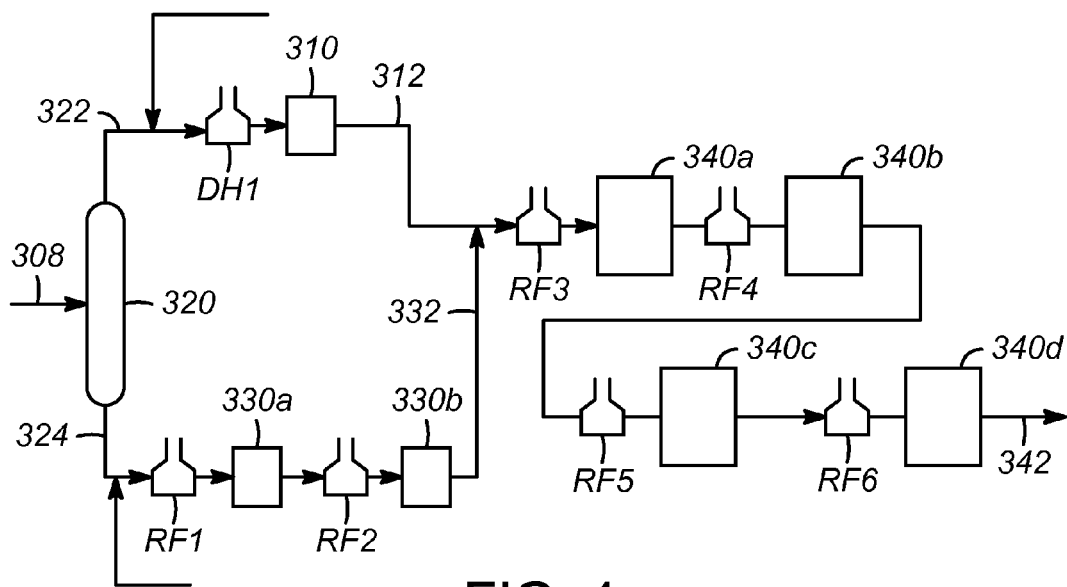


FIG. 4

1

# INITIAL HYDROTREATING OF NAPHTHENES WITH SUBSEQUENT HIGH TEMPERATURE REFORMING

## FIELD OF THE INVENTION

The present invention relates to the process of enhancing the production of aromatic compounds. In particular the improvement and enhancement of aromatic compounds such as benzene, toluene and xylenes from a naphtha feedstream through high temperature reforming.

## BACKGROUND OF THE INVENTION

The reforming of petroleum raw materials is an important process for producing useful products. One important process is the separation and upgrading of hydrocarbons for a motor fuel, such as producing a naphtha feedstream and upgrading the octane value of the naphtha in the production of gasoline. However, hydrocarbon feedstreams from a raw petroleum source include the production of useful chemical precursors for use in the production of plastics, detergents and other products.

The upgrading of gasoline is an important process, and improvements for the conversion of naphtha feedstreams to increase the octane number have been presented in U.S. Pat. No. 3,729,409, U.S. Pat. No. 753,891, U.S. Pat. No. 767,568, U.S. Pat. No. 839,024, U.S. Pat. No. 882,040 and U.S. Pat. No. 242,576. These processes involve a variety of means to enhance octane number, and particularly for enhancing the aromatic content of gasoline.

While there is a move to reduce the aromatics in gasoline, aromatics have many important commercial uses. Among those commercial uses include the production of detergents in the form of alkyl-aryl sulfonates, and plastics. These commercial uses require more and purer grades of aromatics. The production and separation of aromatics from hydrocarbons streams are increasingly important.

Processes include splitting feeds and operating several reformers using different catalysts, such as a monometallic catalyst or a non-acidic catalyst for lower boiling point hydrocarbons and bi-metallic catalysts for higher boiling point hydrocarbons. Other improvements include new catalysts, as presented in U.S. Pat. No. 4,677,094, U.S. Pat. No. 6,809,061 and U.S. Pat. No. 7,799,729. However, there are limits to the methods and catalysts presented in these patents, and which can entail significant increases in costs.

Improved processes are needed to reduce the costs and energy usage in the production of aromatic compounds.

## SUMMARY OF THE INVENTION

The present invention has found that the production of aromatics from a hydrocarbon stream, such as a full boiling range naphtha, with a substantial amount of naphthenic compounds. Processing the feedstream, or a portion of the feedstream, to reduce the naphthenes to aromatics before reforming the process stream reduces the energy load on the reforming units and increases the aromatics content in the product stream.

The process separates the hydrocarbon feedstream into two streams, one with an increased naphthene content, and one with a reduced naphthene content. The process includes passing the hydrocarbon feedstream to a fractionation unit to generate an overhead stream and a bottoms stream. The overhead stream comprises C7 and lighter hydrocarbons, including naphthenes, and the bottoms stream comprises C8 and

2

heavier hydrocarbons. The overhead stream is passed to a dehydrogenation unit to generate a dehydrogenated stream with a reduced naphthene content. The bottoms stream is passed to a first reactor system to generate a first effluent stream. The first effluent stream and the dehydrogenated stream are passed to a second reforming reactor system to generate an aromatics effluent stream. The aromatics effluent stream is passed to a reformat splitter to generate an overhead stream comprising C7 and lighter aromatics and hydrocarbons, and a bottoms stream comprising C8 and heavier hydrocarbons. The reformat overhead stream is passed to an aromatics recovery unit to generate an aromatics product stream comprising benzene and toluene.

Other objects, advantages and applications of the present invention will become apparent to those skilled in the art from the following detailed description and drawings.

## BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 shows one embodiment of the present invention with a dehydrogenation reactor applied to the total feed, followed by reforming reactors;

FIG. 2 shows a second invention where a hydrocarbon stream is dehydrogenated before passing the streams on to the reforming reactor system and the dehydrogenated stream is separated and reformed;

FIG. 3 shows another embodiment with a dehydrogenation reactor applied to the light ends of a fractionated feed; and

FIG. 4 shows a specific configuration with a six reactor system.

## DETAILED DESCRIPTION OF THE INVENTION

The reforming of a hydrocarbon feedstream to increase the aromatics content is important for enhancing the value of the hydrocarbon stream. Aromatics, such as benzene and toluene are high value chemicals and are used in a variety of processes to generate downstream products. Examples include alkylaromatic compounds for detergents, ethyl benzene and cumene. The reforming process can include endothermic reactions and can affect the efficiency due to process control of the temperatures of the reactors.

The present invention is directed to improving the yields of aromatics from a hydrocarbon feedstream. In particular, the improvement is for a full boiling range naphtha feedstream where the hydrocarbons are reformed to increase the yields of aromatics in the C6 to C8 range. The new process is designed to utilize a multiple reactors, controlled at different conditions to maximize paraffin cyclization and aromatization, but also minimize metal-catalyzed coking and thermal cracking. Due to problems associated with high inlet temperatures, it is desirable to maximize the catalyst bed temperatures while minimizing the reactor inlet temperatures. Due to the endothermic nature of some of the components in a naphtha feed, the usual approach is to heat the feed to a greater temperature, as the temperature will drop in the reactor.

It is significant to note that in studying the reforming process, it is generally known that larger paraffins, such as C8 and larger, aromatize more readily than C6 paraffins. This would lead to the belief that the lighter hydrocarbons would benefit from longer residence times in the reactor than larger paraffins. Contrary to this, it was found that applying shorter contact times for the lighter hydrocarbons than for the heavier hydrocarbons produced greater overall conversion yields. This leads to new ideas on the process control that are counter-intuitive to the accepted reforming process.

The present invention seeks to improve the energy savings of the reforming process of a hydrocarbon feedstream in the production of aromatic compounds. The process, as shown in FIG. 1, includes passing a hydrocarbon feedstream **8** to a first reactor **10** to generate a dehydrogenated hydrocarbon stream **12**. The first reactor is for hydrotreating the naphthenic compounds, and can be either a dehydrogenation reactor, or a reforming reactor. When the first reactor is a reforming reactor, the same catalyst can be used in each of the reforming reactors in the process described herein. The dehydrogenated stream **12** is passed to a second reactor system **20** to generate a reformed hydrocarbon stream **22** having an increased aromatics content. The second reactor system is preferable a reforming reactor system that is operated at substantially isothermal conditions. The reforming reactor system **20** cyclizes and aromatizes the paraffinic compounds. The dehydrogenated hydrocarbon stream has a reduced naphthene content, and allows for lower energy input to subsequent reactors, and allows for operating the isothermal reactor system **20** at an increased temperature while minimizing the temperature drop in the reactors. The reformed hydrocarbon stream **22** is passed to a reformat splitter **30** to generate a reformat overhead stream **32** having C6 and C7 aromatics, and a reformat bottoms stream **34** having heavier hydrocarbons. The reformat overhead is passed to an aromatics separation unit **40** to generate an aromatics product stream **42** and a raffinate stream **44**. The raffinate stream **44** can be directed back to the reforming reactor system **20** to further cyclize and aromatize the paraffins in the raffinate stream **44**.

The aromatics recovery unit **40** can comprise different methods of separating aromatics from a hydrocarbon stream. One industry standard is the Sulfolane™ process, which is an extractive distillation process utilizing sulfolane to facilitate high purity extraction of aromatics. The Sulfolane™ process is well known to those skilled in the art.

The dehydrogenation reactor system **10** can comprise a plurality of reactors, where each reactor is operated at a temperature between 200° C. and 650° C., with a preferred operation temperature between 440° C. and 560° C. Operational conditions for the dehydrogenation reactor include a pressure between 100 kPa and 10 MPa, with a preferred pressure between 100 kPa and 2 MPa, and with a more preferred pressure between 100 kPa and 500 kPa. The dehydrogenation reactor system **10** can include a recycle hydrogen gas stream for the dehydrogenation process.

The substantially isothermal reactor system **20** comprises a plurality of reactors with inter-reactor heaters, and can include a temperature step up reactor system, where first one or two reactors in the system are operated at a lower temperature, with the remainder of the reactors operated at higher temperatures. The reactors are operated in a series arrangement, where the process stream flows through each reactor, and is reheated to the same inlet reactor temperature for each reactor. The reforming reactor system **20** is preferably operated at a temperature of at least 540° C., with the reforming reaction temperature conditions between 540° C. and 600° C., and more preferably between 560° C. and 580° C.

When the reforming system **20** is operated in a temperature step up mode, the first reactor, or first and second reactors, are operated at a temperature between 440° C. and 560° C., and the subsequent reactors operated at a temperature greater than 540° C. Preferably the first reactor is operated at a temperature between 440° C. and 460° C., with the subsequent reactors operated at a temperature between 550° C. and 570° C. One optional operation of the reforming reactor system **20** is to operate each subsequent reactor at a higher temperature than the previous reactor in the series.

In addition to the operational temperatures, the processing conditions of the different reformers allows for different operational control. Additional variables that are controllable include the space velocities, the hydrogen to hydrocarbon feed ratios, and the pressures. It is preferred that the pressure in the reformer with the lighter hydrocarbons is operated at a lower pressure than in the reformer with the heavier hydrocarbons. An example for operating pressures for the first reformer are from 130 kPa to 310 kPa with a preferred pressure of around 170 kPa (10 psig), and operating pressures for the second reformer are from 240 kPa to 580 kPa with a preferred pressure of around 450 kPa (50 psig).

The simulation of a commercial reactor included an inlet temperature of 515° C. to 560° C., a hydrogen to hydrocarbon ratio of 5, pressures in the reactor at different levels from 10 to 50 psig, or 170 to 450 kPa, the WHSV ranged from 0.75 hr<sup>-1</sup> to 3 hr<sup>-1</sup>, and with different catalyst loadings to expand the conversion range.

The reformat splitter **30** can be operated to change the mix of aromatics in the overhead stream **32**. For an increase in xylene recovery, the reformat splitter **30** can be operated to send C8 aromatics into the overhead stream **32**, and to the subsequent aromatics recovery unit **40**.

The process for another invention comprises passing a portion of a hydrocarbon feedstream, as shown in FIG. 2. In particular, a naphtha feedstream **108** is dehydrogenated in a dehydrogenation reactor **110** to generate a naphtha feedstream having a reduced naphthene content **112**. The reduced naphtha stream **112** is passed to a fractionation unit **120** to generate a light overhead stream **122** comprising C7 and lighter hydrocarbons, and a heavy bottoms stream **124** comprising C8 and heavier hydrocarbons. The bottoms stream **124** is passed to a first reformer reactor system **130** to generate a first reformat stream **132** having an increased aromatics content. The first reformat stream **132** and the light overhead stream **122** are passed to a second reformer reactor system **140** to generate a second reformat stream **142** comprising aromatics. The second reformer reactor system **140** is operated as a substantially isothermal reactor system, and is operated at a high temperature. In an alternate embodiment, the reactor **110** can comprise a reforming reactor instead of a dehydrogenation reactor.

In one embodiment, the reduced naphtha stream **112** is passed to an off-gas separator (not shown) to remove light off-gases, such as hydrogen, and any residual acid gases, such as hydrogen sulfide, that is generated in the dehydrogenation reactor **110**, before passing the naphtha stream **112** to the fractionation unit **120**. The second reformat stream **142** is passed to a reformat splitter **150** to generate a reformat overhead stream **152** comprising C6 and C7 aromatics and lighter hydrocarbons, and a reformat bottoms stream **154** comprising C8 and heavier hydrocarbons. The reformat overhead stream **152** is passed to an aromatics recovery unit **160** to generate an aromatics product stream **162** and a raffinate stream **164**. The aromatics product stream **162** will comprise benzene and toluene, and small amounts of xylenes. Optionally, the reformat splitter **150** can be operated to recover C8 aromatics in the reformat overhead stream **152** and subsequently in the aromatics product stream **162**.

The first reformer reactor system **130** can comprise a plurality of reactors with inter-reactor heaters. In a preferred embodiment, the reactors are in a series relationship, with the first reformer reactor system **130** comprises two reactors with each reactor having a reactor feed heater. The first reactor is operated at a lower temperature and at conditions to convert the most endothermic hydrocarbons to aromatics. The first reactor product is heated to a higher inlet temperature for the

second reactor. Temperatures for the first reactor have an inlet temperature between 440° C. and 560° C., with a preferred inlet temperature between 440° C. and 460° C., with a more preferred temperature between 445° C. to 455° C., and a most preferred inlet temperature of 450° C. Temperatures for the second reactor have an inlet temperature between 540° C. and 580° C., with a preferred inlet temperature of 560° C. The second reformer reactor system **140** can comprise a plurality of reactors in a series relationship with inter-reactor heaters. When operated in conjunction with the first reactor system **130**, the second reactor system **140** is operated to control the temperature so as to minimize temperature variation. In particular, the reactions are endothermic, so the inter-reactor heaters are operated to heat the reactor inlet temperatures to between 540° C. and 580° C., with a preferred inlet temperature of 560° C.

In one embodiment, the raffinate stream **164** is passed to the first reactor in the first reactor system **140**, to cyclize and aromatize the more endothermic components, before passing the first reactor effluent on to a subsequent reactor.

One specific embodiment includes passing a naphtha feedstream **108** and a hydrogen rich recycle gas to the dehydrogenation reactor **110** to reduce the naphthenic content of the naphtha feedstream **108**. The reduced stream **112** is passed to a fractionation unit **120** to generate a C7 and lower hydrocarbon stream **122**, and a C8 and heavier hydrocarbon stream **124**. The C8 and heavier hydrocarbon stream **124** is passed with recycle gas to a first reactor system **130** to generate a first reactor effluent stream **132**. The first reactor effluent stream **132** and the C7 and lower hydrocarbon stream **122** are passed to a second reactor system **140** to generate a second reactor effluent stream **142**. The second reactor effluent stream **142** is passed to a reformate splitter **150** to generate a reformate overhead **152** and a reformate bottoms stream **154**. The reformate overhead **152** comprises C6 and C7 aromatics and is passed to an aromatics recovery unit **160** to generate an aromatics product stream **162** and a raffinate stream **164**. The raffinate stream **164** is passed to the dehydrogenation reactor **110** to react the olefins and reduce the amount of olefins passed to the reforming reactor systems **130** and **140**.

In another embodiment, the process for increasing the aromatics yields from a hydrocarbon feedstream includes passing the hydrocarbon stream to a dehydrogenation reactor. The dehydrogenated stream is passed to a separator to create a light hydrocarbon stream comprising C7 and lighter hydrocarbons, and a heavy hydrocarbon stream comprising C8 and heavier hydrocarbons. The light stream is passed to a first reforming reactor system to generate a first reformate stream, comprising C6 and C7 aromatic compounds. The heavy stream is passed to a second reforming reactor system to generate a second reformate stream comprising aromatic compounds. The first and second reformate streams are passed to a reformate splitter to generate an overhead stream comprising C7 and lighter aromatics and hydrocarbons, and a bottoms stream comprising C8 and heavier aromatics and hydrocarbons.

The invention for increasing the yields of aromatics from a hydrocarbon feedstream involves improving the approach for reforming the hydrocarbon feedstream. While the process of reforming a hydrocarbon feedstream is known, and one of the issues is the endothermic nature of the process, there is no information that teaches one can improve the yields, while reducing energy consumption by an innovative method of processing the hydrocarbon stream. The process, as shown in FIG. 3, involves passing the hydrocarbon feedstream **208** to a fractionation unit **220**. The feedstream is separated into a light overhead stream **222** and a heavier bottoms stream **224**. The

light overhead stream **222** comprises C7 and lighter hydrocarbons and is passed to a dehydrogenation reactor **210** where a dehydrogenated stream **212** having a reduced naphtene content is generated. The bottoms stream **224**, comprising C8 and heavier hydrocarbons, is passed to a first reforming reactor system **230** to generate a first reactor effluent stream **232**. The first effluent stream **232** and the dehydrogenated stream **212** are passed to a second reactor system **240** to generate an aromatics effluent stream **242**.

In an alternate embodiment to the process as shown in FIG. 3, the reactor **210** can comprise a reforming reactor instead of a dehydrogenation reactor. The benefit of using a reforming reactor, operated at a lower temperature, provides for the use of the same catalyst in all of the reforming reactors.

The process can further include passing the aromatics effluent stream **242** to an aromatics splitter **250** to generate an aromatics overhead stream **252** having C7 and lighter aromatics, and a bottoms stream **254** having heavier hydrocarbons. The aromatics overhead stream **252** is passed to an aromatics separation unit **260** to generate an aromatics product stream **262** and a raffinate stream **264**. The raffinate stream **264** can have a substantial amount of olefins in the raffinate, and can be passed to the dehydrogenation reactor **210** for further processing of the olefins and conversion to aromatics. When the raffinate stream **264** is low in olefin content, the raffinate stream **264** can bypass the dehydrogenation reactor and be passed to the second reactor system **240**.

The first reactor system **230** can include a plurality of reactors, where each reactor has a heater for heating the incoming process fluid to a desired reaction temperature. The reactors are operated in a series arrangement, with inter-reactor heaters. In the first reactor system **230**, the first reactor within the system **230**, the first reactor is operated at an inlet temperature between 440° C. and 560° C., and preferably between 440° C. and 460° C. Subsequent reactors in the first reactor system are operated with an inlet reactor temperature between 540° C. and 580° C., and preferably with an inlet temperature between 560° C. and 580° C.

The second reactor system **240** can include a plurality of reactors in a series arrangement, with each reactor having a heater for controlling the inlet temperature of the processing fluid. The inlet temperature for each reactor is in the temperature range from 540° C. to 580° C., with a preferred range from 560° C. to 580° C., and with a more preferred control of the inlet temperature to 560° C.

Using microreactor results, and simulations, the heat and weight balances for reactor configurations were tested. FIG. 4 shows a combination of six reactor beds with a dehydrogenation reactor **310** for treating the overhead stream **322** from the fractionation unit **320**. The six reactor beds are in a 2×4 configuration with 2 reactors in the first reactor system, and 4 reactors in the second reactor system. A comparison of heat and weight balance results and reformate yields for the naphtha reforming processes was performed between this case and a case where there was no dehydrogenation reactor **310**. Each reactor has a feed heater, where the feed into each reactor was raised to a preferred temperature. In the process, the naphtha feed **308** is split to produce an overhead stream **322** rich in C7 naphthenes and lighter components and a bottoms stream **324** rich in C8 and heavier components. The bottoms stream **324** is fed to the first reforming catalyst reactor **330a**, with the effluent from the first reforming reactor **330a** fed to the second reforming reactor **330b** to generate a first stream **332**. The overhead stream **322** is fed to the dehydrogenation reactor **310** to generate the dehydrogenated effluent stream **312**. The dehydrogenated stream **312** and the first stream **332** are combined and heated in RF3 to be fed to the third reforming

7

reactor **340a**. The process stream subsequently passed through the subsequent reactor feed heaters RF4, FR5, RF6 and subsequent reactors **340b**, **340c**, and **340d** as shown in FIG. 4.

TABLE 1

Reforming Reactor Inter-Heater Duty (MM Btu/hr)		
	Split Naphtha Feed and 2 × 4 Series Flow Reforming Section	Split Naphtha Feed with Light Naphtha Dehydro and 2 × 4 Series Flow Reforming Section
Reactor 2 Feed Heater	133.10	132.70
Reactor 3 Feed Heater	120.00	119.80
Reactor 4 Feed Heater	83.29	69.19
Reactor 5 Feed Heater	51.65	44.28
Reactor 6 Feed Heater	29.02	24.16

The 2+4 reforming reactor section comprises six reactors in series, with the heavy hydrocarbon stream passing through the first two reactors, and with the light hydrocarbon stream merging with the second reactor effluent and passing through the remaining 4 reactors. The heat duties are in MM Btu/hr.

From the results, the process that includes the naphthene dehydrogenation upstream of the reforming reactors results in a lower heat duty for inter-reactor heaters (RF3, RF4, RF5 and RF6). In addition, the following Table 2, shows the dehydrogenation pre-treatment of the naphtha feedstream results in a reduced temperature drop in the reactors. This is due to the reduction in the reaction endotherm in the reactor beds due to a reduction in the amount of naphthenes passing to the reforming reactors. This provides for keeping the system nearer to an isothermal process, with the reactions held nearer to the desired reaction temperature.

TABLE 2

Reforming Zone Reaction Conditions						
	Split Naphtha Feed and 2 × 4 Series Flow Reforming Section			Split Naphtha Feed with Light Naphtha Dehydro and 2 × 4 Series Flow Reforming Section		
	R × R vol.	R × R inlet	R × R outlet	R × R vol.	R × R inlet	R × R outlet
Reactor 1	13.11	449	417	13.11	449	417
Reactor 2	18.12	560	475	18.12	560	475
Reactor 3	17.53	560	497	17.53	560	507
Reactor 4	18.75	560	520	18.75	560	527
Reactor 5	19.28	560	538	19.28	560	542
Reactor 6	19.43	560	549	19.43	560	551

Reactor volume (R×R vol.) is in cubic meters, and temperatures are in degrees Celsius. The inlet temperature for the first reactor is 449° C. and for the remaining reactors is 560° C.

While this provides a significant energy savings, there is an improvement in the conversion of the naphtha feed to aromatics by maintaining higher reactor temperatures. Table 3 shows the increase in the yields of benzene (A6) and toluene (A7) with the inclusion of the dehydrogenation reactor **310**. The improvement in yields are due in part to the higher overall reactor temperatures in the reforming reactors.

8

TABLE 3

Reformate Composition and Aromatics Yields			
Split Naphtha Feed and 2 × 4 Series Flow Reforming Section		Split Naphtha Feed with Light Naphtha Dehydro and 2 × 4 Series Flow Reforming Section	
Net Reformate		Net Reformate	
H2, %	3.8	H2, %	3.9
C1-C5, %	16.5	C1-C5, %	16.7
C6-C10, %	79.7	C6-C10, %	79.3
C11+, %	0.1	C11+, %	0.1
P6 Conversion w/w	0.627	P6 Conversion w/w	0.610
P7 Conversion w/w	0.989	P7 Conversion w/w	0.982
P8 Conversion w/w	0.998	P8 Conversion w/w	0.998
Net Reformate Aromatics		Net Reformate Aromatics	
A6-A7, %	25.2	A6-A7, %	25.9
PX, w/w	0.032	PX, w/w	0.032
Total A6-A10	68.2	Total A6-A10	68.9

The results of two simulations showing the improvement is shown in Tables 4 and 5. A base case was run, and compared against the new configuration.

TABLE 4

Same amount of catalyst		
	Base case	Case 1
Reactor inlet temp, deg. C.	560	468 and 560
C7 paraffin conversion, w/w %	97.8%	97.9%
Total catalyst volume, m3	121.8	121.8
Net Yield (A7-A10), w/w %	52.4%	52.9%
Net Yield (C1-C4), w/w %	15.1%	14.8%
Net Yield, H2, w/w %	3.8%	3.8%

The cases presented in Table 3 include the new configuration, Case 1, against a base case. The base case involved the use of a reforming reactor system operated at a high temperature. In the base case, there were four reforming reactors with the inlet temperature of 560° C. The new configuration in Case 1, involved the reforming reactor system of the base case, with a pre-reactor. The pre-reactor was a reforming reactor operated at 468° C. The total amount of catalyst for both the base case and the new configuration was the same, where the catalyst was redistributed, such that each reactor in the new configuration has a smaller amount of catalyst. The process shows an increase in the yields of aromatics, while also having the added benefit of a decrease in yields of light ends. The net yield is equal to the net outlet minus the fresh feed divided by the fresh feed, or:

$$(\text{Net Yield}) = (\text{Net Outlet} - \text{Fresh Feed}) / (\text{Fresh Feed}).$$

A second simulation was run to show the improvement allows for a reduction in the amount of catalyst necessary to show improved yields.

TABLE 5

Reduced catalyst		
	Base case	Case 2
Reactor inlet temp, deg. C.	560	454 and 560
C7 paraffin conversion, w/w %	97.8%	97.8%
Total catalyst volume, m3	121.8	84.95



TABLE 5-continued

Reduced catalyst		
	Base case	Case 2
Net Yield (A7-A10), w/w %	52.4%	54.1%
Net Yield (C1-C4), w/w %	15.1%	13.2%
Net Yield, H <sub>2</sub> , w/w %	3.8%	4.0%

The reduced catalyst shows there is improvement with using less catalyst. In case 2, the total amount of catalyst for all the reactors is over 30% less than the total amount of catalyst for the base case. In case 2, there were seven reactors operated at the high temperature of 560° C., and the pre-reactor operated at 454° C. The total catalyst was distributed over all of the reactors. The lower temperature in the pre-reactor provides the benefit of lower catalyst volume in the downstream reactors operated at the elevated temperature. The new process also has a higher space velocity, which reduces secondary reactions and also contributes to improved operations.

The reforming reactions were operated with a platinum catalyst. The platinum catalyst needs some metal passivation for the prevention of metal catalyzed coking during the process. The metal passivation is performed through the addition of a small amount of sulfur. The sulfur in the reactor is usually provided by hydrogen sulfide (H<sub>2</sub>S). The H<sub>2</sub>S addition to the process is generated through the addition of DMDS (dimethyl disulfide) upstream of the reactors. The DMDS thermally decomposes during the heating of the feedstream. However, the DMDS is not entirely decomposed to H<sub>2</sub>S and some of the DMDS enters the reactors, and prematurely deactivates some of the catalyst in the high temperature process. An unexpected benefit with the new process includes the total decomposition of the DMDS to H<sub>2</sub>S in the pre-reactor, and thereby protects the catalyst in the high temperature reforming reactors.

Therefore, increases can be achieved through innovative flow schemes that allow for process control of the reactions. While the invention has been described with what are presently considered the preferred embodiments, it is to be understood that the invention is not limited to the disclosed embodiments, but it is intended to cover various modifications and equivalent arrangements included within the scope of the appended claims.

The invention claimed is:

1. A process for increasing the yields of aromatics from a hydrocarbon feedstream, comprising:

passing the hydrocarbon feedstream to a fractionation unit to generate an overhead stream comprising C7 and lighter hydrocarbons, and a bottoms stream comprising C8 and heavier hydrocarbons;

passing the overhead stream to a dehydrogenation reactor to dehydrogenate naphthenes and generate a dehydrogenated stream having a reduced naphthenic content;

passing the bottoms stream to a first reforming reactor system to generate a first reactor effluent having an increased aromatic content, wherein the first reforming reactor system is operated at an inlet temperature between 440° C. and 560° C.;

passing the first reactor effluent to a second reforming reactor system, and the dehydrogenated overhead stream to the second reforming reactor system to generate an aromatics effluent stream, wherein the second reactor system is operated at an inlet temperature between 540° C. and 580° C. and a pressure less than 580 kPa.

2. The process of claim 1 further comprising:

passing the aromatics effluent stream to an aromatics splitter to generate an aromatics overhead having C7 and lighter aromatics, and a bottoms stream; and

passing the aromatics overhead stream to an aromatics separation unit to generate an aromatics product stream and a raffinate stream.

3. The process of claim 1 wherein the hydrocarbon feedstream comprises a full boiling range naphtha.

4. The process of claim 1 wherein the first reforming reactor system comprises a plurality of reactors.

5. The process of claim 4 wherein the plurality of reactors comprises a heater for each reactor to heat the reactor feedstream.

6. The process of claim 4 wherein the first reactor of the first reforming reactor system is operated at an inlet temperature between 440° C. and 560° C., and the subsequent reactors of the first reactor system are operated at inlet temperatures between 540° C. and 580° C.

7. The process of claim 4 wherein the plurality of reactors are in series with inter-reactor heaters.

8. The process of claim 1 wherein the second reforming reactor system comprises a plurality of reactors.

9. The process of claim 1 further comprising:

passing the aromatics effluent stream to a reformate splitter to generate a reformate splitter overhead stream comprising C7 and C6 aromatics, and a reformate splitter bottoms stream comprising C8 and heavier aromatics; and

passing the reformate splitter overhead stream to an aromatics separation unit thereby generating an aromatics product stream and a raffinate stream.

10. The process of claim 9 further comprising passing the raffinate stream to the dehydrogenation reactor.

11. A process for increasing the yields of aromatics from a hydrocarbon feedstream, comprising:

passing the hydrocarbon feedstream to a fractionation unit to generate an overhead stream comprising C7 and lighter hydrocarbons, and a bottoms stream comprising C8 and heavier hydrocarbons;

passing the overhead stream and a recycle gas to a dehydrogenation reactor to generate a dehydrogenated overhead stream;

passing the bottoms stream and a portion of the recycle gas to a first reforming reactor system to generate a first reactor effluent having an increased aromatic content;

passing the first reactor effluent to a second reforming reactor system, and the dehydrogenated overhead stream to the second reforming reactor system to generate an aromatics effluent stream, wherein the second reforming reactor is operated at an inlet temperature greater than or equal to a first reforming reactor inlet temperature and wherein the second reforming reactor system is operated at an inlet temperature greater than 540° C. and a pressure less than 580 kPa; and

passing the aromatics effluent stream to a reformate splitter to generate a reformate splitter overhead stream comprising C7 and C6 aromatics, and a reformate splitter bottoms stream comprising C8 and heavier aromatics; and

passing the reformate splitter overhead stream to an aromatics separation unit thereby generating an aromatics product stream and a raffinate stream.

12. The process of claim 11 further comprising passing the raffinate stream to the dehydrogenation reactor.

13. The process of claim 11 wherein the hydrocarbon feedstream is a full boiling range naphtha.

**11**

**14.** The process of claim **11** wherein the first reforming reactor system comprises at least two reactors, and where the first reactor in the first reforming reactor system is operated at an inlet temperature between 440° C. and 460° C., and wherein the subsequent reactors in the first reforming reactor system are operated at inlet temperatures between 540° C. and 580° C. 5

**15.** The process of claim **11** wherein the second reforming reactor system comprises a plurality of reactors and inter-reactor heaters. 10

**16.** The process of claim **11** wherein the second reforming reactor system is operated at an inlet temperature between 540° C. and 580° C.

\* \* \* \* \*

**12**